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EFFECT OF THE COMPOSITION OF PHOSPHORUS-CONTAINING RAW MATERIALS ON GLASS FORMATION IN THE $Li_2O – Li_2SO_4 – P_2O_5$ SYSTEM

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Calculation and experimental methods showed that the use of lithium metaphosphate for making up batches of $Li_2O – Li_2SO_4 – P_2O_5$ multilithium glass systems reduces the founding temperature-time parameters while simultaneously increasing the homogeneity of the melts.

When glasses are used as solid electrolytes for chemical current sources, most of the compositions of these glasses are based on the glass-forming systems $Li_2O – B_2O_3$ and $Li_2O – P_2O_5$ [1, 2]. To increase the conductivity of these glasses with respect to lithium ions, oxygen-containing lithium salts (including Li_2SO_4) are added to their composition [3, 4]. It was noted in [5] that the ion conductivity of glasses of the $Li_2O – Li_2SO_4 – B_2O_3$ system is directly proportional to the lithium oxide content. The compositions of vitreous solid electrolytes with maximum lithium ion conductivity of up to 3.1×10^{-6} S · cm^{-1} (RF patent No. 011032) are in the crystallization field of the compound $3Li_2O \cdot B_2O_3$, which incoherently melts at the temperature of 715°C [7]. For this reason, the founding temperature of glasses of this composition does not exceed 950°C. Synthesis of monolithic glasses of similar composition in the $Li_2O – Li_2SO_4 – P_2O_5$ system involves great difficulties, since the crystalline compound $3Li_2O \cdot P_2O_5$ melts at a much higher temperature (1220°C) [7].

In making up phosphate glass batches, phosphorus oxide is usually added to them with ammonium phosphate or orthophosphoric acid [8, 9]. Due to the high volatility of P_2O_5, batches of the corresponding composition are first treated with heat at low temperatures for a long time, which significantly slows the founding process.

We investigated the effect of the composition of phosphorus-containing raw materials on the glass-forming power of melts with a high lithium oxide content in the $Li_2O – Li_2SO_4 – P_2O_5$ system.

The following raw materials were used in conducting the experimental studies: lithium carbonate (cp), lithium sulfate, orthophosphoric acid, ammonium phosphate, and lithium metaphosphate.

X-ray phase analysis of the materials obtained was performed on a DRON-3.0 x-ray instrument (CoK_α radiation, 35 kW, 10 mA).

The liquidus line calculated with the Epstein – Howland method for the pseudobinary systems $xLi_2O \cdot P_2O_5 – Li_2SO_4$ [10] showed that for a 10 – 20%[2] Li_2SO_4 content, increasing the $Li_2O : P_2O_5$ ratio from 1 to 3 was accompanied by a sharp increase in the liquidus temperature of the materials — from approximately 650 to 1200°C (Fig. 1).

We can hypothesize that heat treatment of batches of the $Li_2O – Li_2SO_4 – P_2O_5$ system with a high lithium oxide content should be accompanied by formation of highly basic lithium phosphates and correspondingly, an increase in the glass melting temperature.

[2] Here and below: molar content.

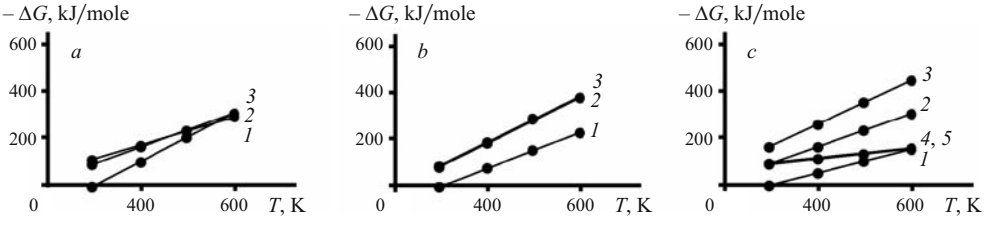

Fig. 1. Isobaric-isothermal potential of the hypothetical reactions that take place in glass batches of the compositions $0.4Li_2O \cdot 0.2Li_2SO_4 \cdot 0.4P_2O_5$ (*a*), $0.5Li_2O \cdot 0.2Li_2SO_4 \cdot 0.3P_2O_5$ (*b*), and $0.6Li_2O \cdot 0.2Li_2SO_4 \cdot 0.2P_2O_5$ (*c*).

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To test this hypothesis, we evaluated the thermodynamic probability of formation of lithium phosphates of different basicity in heat treatment of glass batches of the compositions $0.4Li_2O \cdot 0.2Li_2SO_4 \cdot 0.4P_2O_5$, $0.5Li_2O \cdot 0.2Li_2SO_4 \cdot 0.3P_2O_5$, and $0.6Li_2O \cdot 0.2Li_2SO_4 \cdot 0.2P_2O_5$ containing lithium carbonate, orthophosphoric acid, and lithium sulfate. In compiling the possible reactions in the batch, we assumed that Li_2SO_4 and lithium phosphate would not form compounds together.

The reactions that hypothetically take place in a glass batch of the composition $0.4Li_2O \cdot 0.2Li_2SO_4 \cdot 0.4P_2O_5$ ($Li_2O : P_2O_5 = 1$) are:

$$2Li_2CO_3 + 4H_3PO_4 + Li_2SO_4 \longrightarrow \begin{cases} 4LiPO_3 + Li_2SO_4 + 2CO_2\uparrow + 6H_2O; \\ Li_4P_2O_7 + 2H_3PO_4 + Li_2SO_4 + 2CO_2\uparrow + 3H_2O; \\ 4/3(Li_3PO_4) + 8/3(H_3PO_4) + Li_2SO_4 + 2CO_2\uparrow + 2H_2O. \end{cases}$$

The reactions that hypothetically take place in a glass batch of the composition $0.5Li_2O \cdot 0.2Li_2SO_4 \cdot 0.3P_2O_5$ ($Li_2O : P_2O_5 \sim 1.7$) are:

$$2{,}5Li_2CO_3 + 3H_3PO_4 + Li_2SO_4 \longrightarrow \begin{cases} 3LiPO_3 + Li_2CO_3 + Li_2SO_4 + 1{,}5CO_2\uparrow + 4{,}5H_2O; \\ Li_4P_2O_7 + LiPO_3 + Li_2SO_4 + 2{,}5CO_2\uparrow + 4{,}5H_2O; \\ Li_3PO_4 + 2LiPO_3 + Li_2SO_4 + 2{,}5CO_2\uparrow + 4{,}5H_2O. \end{cases}$$

The reactions that hypothetically take place in a glass batch of the composition $0.6Li_2O \cdot 0.2Li_2SO_4 \cdot 0.2P_2O_5$ ($Li_2O : P_2O_5 = 3$) are:

$$3Li_2CO_3 + 2H_3PO_4 + Li_2SO_4 \longrightarrow \begin{cases} 2LiPO_3 + 2Li_2CO_3 + Li_2SO_4 + CO_2\uparrow + 3H_2O; & (1) \\ Li_4P_2O_7 + Li_2CO_3 + Li_2SO_4 + 2CO_2\uparrow + 3H_2O; \\ 2Li_3PO_4 + Li_2SO_4 + 3CO_2\uparrow + 3H_2O; \end{cases}$$

$$2LiPO_3 + Li_2CO_3 \rightarrow Li_4P_2O_7 + CO_2\uparrow;$$

$$LiPO_3 + 2Li_2CO_3 \rightarrow Li_3PO_4 + 2CO_2\uparrow. \qquad (2)$$

In performing the calculations, we used the thermodynamic constants of the substances reported in [7] (see Table 1).

The results of the calculations of the isobaric-isothermal potential ΔG of the hypothetical reactions performed with the standard method in [10] are shown in Fig. 1.

The calculations showed that the probability of formation of trilithium phosphate increases with an increase in the lithium oxide content in the batch compositions made with orthophosphoric acid. When the batches are dried, the probability of formation of dilithium phosphate is also high.

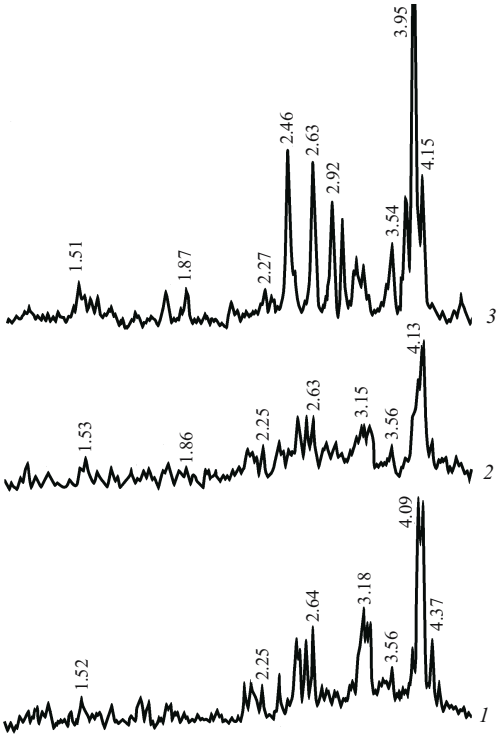

Fig. 2. X-ray patterns of glass batches obtained as a result of mixing lithium carbonate and ammonium sulfate with orthophosphoric acid and subsequent drying: *1*) $0.4Li_2O \cdot 0.2Li_2SO_4 \cdot 0.4P_2O_5$; *2*) $0.5Li_2O \cdot 0.2Li_2SO_4 \cdot 0.2P_2O_5$; *3*) $0.6Li_2O \cdot 0.2Li_2SO_4 \cdot 0.2P_2O_5$.

The x-ray patterns of the glass batches of the investigated compositions obtained as a result of mixing a mixture of lithium carbonate and ammonium sulfate with orthophosphoric acid and then drying (under 300°C) are shown in Fig. 2.

The crystalline compounds $LiPO_3$ ($d = 4.73$, 3.57, 3.27 Å) and $Li_4P_2O_7$ ($d = 4.33$, 3.22, 3.16 Å) according to ASTM data were identified in the x-ray pattern of the glass batch of the composition $0.4Li_2O \cdot 0.2Li_2SO_4 \cdot 0.4P_2O_5$ together with unreacted Li_2SO_4 ($d = 4.73$, 3.57, 3.27 Å). Similar compounds were also identified in the glass batch of the composition $0.5Li_2O \cdot 0.2Li_2SO_4 \cdot 0.3P_2O_5$. The amorphous halo observed in both x-ray patterns could be due to the appearance of lithium hydrophosphates capable of glass formation in the low-temperature region.

The products of heat treatment of the glass batch of the composition $0.6Li_2O \cdot 0.2Li_2SO_4 \cdot 0.2P_2O_5$ also contained $Li_4P_2O_7$ and a small amount of $LiPO_3$ together with the basic crystalline lithium orthophosphate phase Li_3PO_4 ($d = 3.97$, 3.80, 3.59, 2.64 Å).

The thermodynamic probability of formation of the crystalline compound Li_3PO_4 as a result of reaction (2) in a glass batch of the composition $0.6Li_2O \cdot 0.2Li_2SO_4 \cdot 0.2P_2O_5$ is several times lower than as a result of reaction (1) — cor-

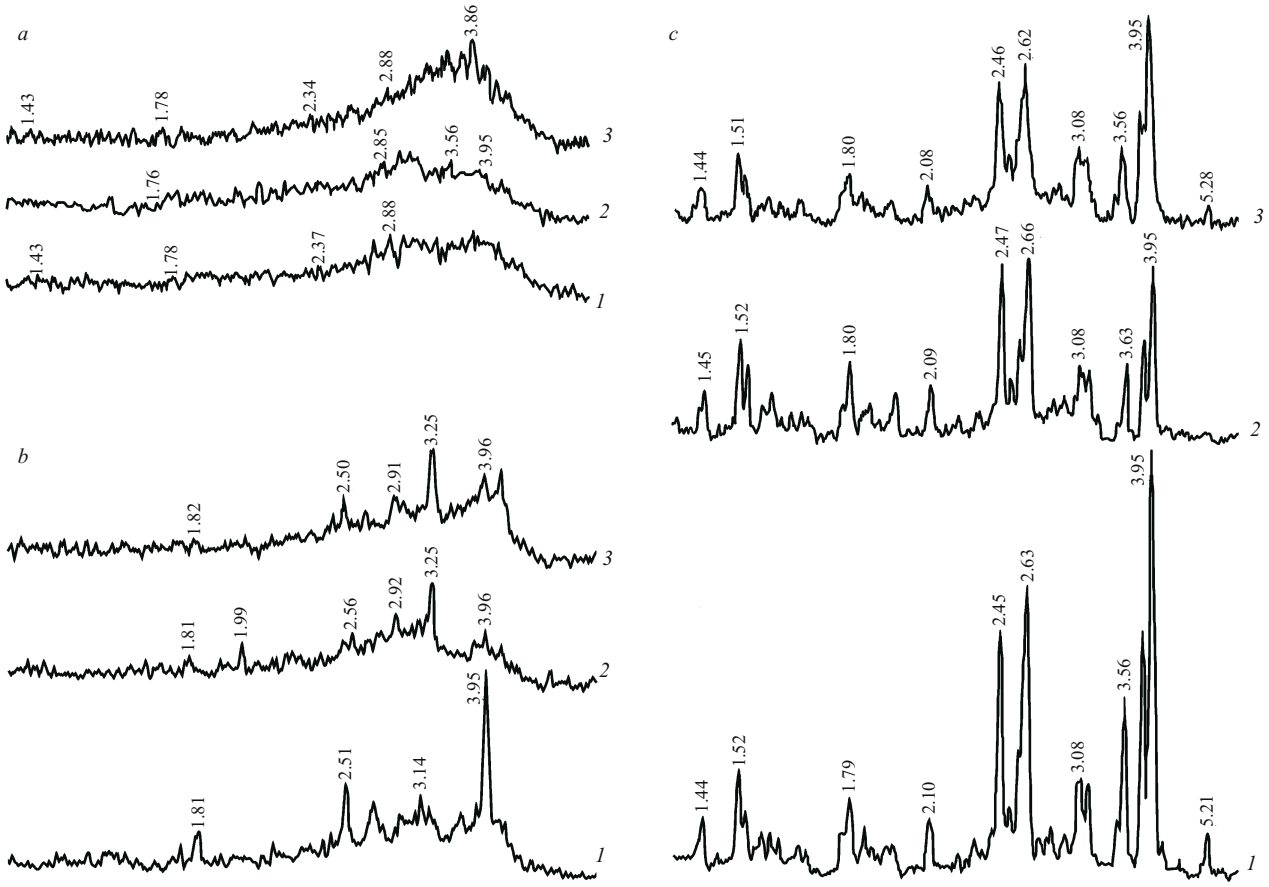

Fig. 3. X-ray patterns of glasses and materials obtained in founding from batches based on orthophosphoric acid (*1*), $(NH_4)_2HPO_4$ (*2*), and vitreous $LiPO_3$ (*3*): *a*) $0.4Li_2O \cdot 0.2Li_2SO_4 \cdot 0.4P_2O_5$; *b*) $0.5Li_2O \cdot 0.2Li_2SO_4 \cdot 0.3P_2O_5$; *c*) $0.6\ Li_2O \cdot 0.2Li_2SO_4 \cdot 0.2P_2O_5$.

respondingly, $\Delta G_{600\,K} = -168.395$ kJ/mole and $\Delta G_{600\,K} = -297.28$ kJ/mole. This suggested that when lithium metaphosphate is used as a raw-material component of glass batches with a Li_2O content greater than 50%, formation of a very high-melting compound — lithium orthophosphate — in the system can be prevented to a significant degree and the melting power of the glasses can be improved. We can also hypothesize that the use of vitreous $LiPO_3$ will make it possible to reduce the founding temperature of the glasses (and consequently reducing volatilization of oxides) due to the appearance of a liquid phase at temperatures below the melting point of crystalline lithium metaphosphate.

In view of the above, we comparatively evaluated the founding power of glasses of the $Li_2O - Li_2SO_4 - P_2O_5$ system with a $Li_2O : P_2O_5$ ratio from 1 to 3 from batches based on orthophosphoric acid, $(NH_4)_2HPO_4$, and vitreous $LiPO_3$.

To obtain vitreous lithium metaphosphate, a batch made up of equimolar quantities of lithium carbonate and ortho-

TABLE 1

Substance (state)	ΔH_{298}, kJ/mole	ΔG_{298}, kJ/mole	S_{298}, J/(mole · K)	Coefficients in the equation $c_p = f(T)$, J/(mole · K)		
				a	$b \times 10^3$	$c \times 10^{-5}$
Li_2CO_3 (cr.)	– 1216.20	– 1132.98	90.42	117.470	10.000	– 20.600
Li_2SO_4 (cr.)	– 1437.89	– 1322.67	114.03	134.161	66.976	– 19.900
H_3PO_4 (l.)	– 1290.12	– 1237.60	176.23	167.860	–	–
$LiPO_3$ (cr.)	– 1255.38	– 1164.29	72.42	98.950	37.660	– 16.340
$Li_4P_2O_7$ (cr.)	– 3358.01	– 3137.85	178.30	222.067	100.464	– 6.475
Li_3PO_4 (cr.)	– 2096.35	– 1966.91	104.65	140.500	50.230	– 3.630
CO_2 (g.)	– 393.69	– 457.38	213.74	44.160	9.040	–
H_2O (g.)	– 241.95	– 185.69	188.79	30.010	10.710	–

phosphoric acid and dried at 300°C was melted in a corundum crucible in a muffle furnace at 800°C. The holding time was 0.5 h. The homogeneous melt was processed by rolling through massive metal rollers, finely ground, and used for making up the batches.

The glass batches of the investigated compositions made from orthophosphoric acid, $(NH_4)_2HPO_4$, and vitreous $LiPO_3$ were melted and processed similar to the lithium metaphosphate. The x-ray patterns of powders of the synthesized materials are shown in Fig. 3.

Visual evaluation of the founding power and x-ray phase studies showed that for glasses with a $Li_2O : P_2O_5$ metaphosphate ratio, the composition of the phosphorus-containing raw material does not affect their homogeneity and melting temperature-time parameters (see Fig. 3*a*). When the $Li_2O : P_2O_5$ ratio in the glass compositions increases to the orthophosphate ratio, the effectiveness of using ammonium phosphate and vitreous lithium metaphosphate for making up the batches for these glasses increases markedly (see Fig. 3*b* and *c*). In particular, using these materials for constituting the batches makes it possible to increase the lithium oxide content in the glass compositions that can be used as solid electrolytes for lithium chemical current sources.

In view of the high volatility of ammonium phosphates, using vitreous ammonium metaphosphate in making up batches of oxide-salt phosphate glasses with a greater than 50% Li_2O content is most effective. The use of such phosphorus-containing raw material not only allows decreasing the glass melting temperature-time parameters but also increasing the homogeneity of the glasses.

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